Experimental Section

NMR spectra were recorded on a Nicolet NT 300 spectrometer in $CDCl_3$ with tetramethylsilane (Me_4Si) as internal standard by using 16K data points and a sweep width of 3412 Hz. Variable temperature spectra were recorded in toluene-d_8 with Me_4Si as internal standard. The NOE experiment was conducted by using a freeze-degassed sample. To minimize the effect of magnetic perturbations, 8 FID's were acquired with the decoupler set at a given frequency. Likewise, 8 FID's were also recorded with the decoupler off resonance. The process was repeated until 1440 pulses had been accumulated for each individual experiment. Subsequent subtraction of the two spectra afforded the net enhancement. A recovery time of 5 s was used. IR spectra were recorded in $CHCl_3$ by using a Perkin-Elmer Model 283 spectrophotometer.

All compounds used in this study were prepared as previously described.[1]

Acknowledgment. Financial support provided by the National Institutes of Health (GM 28128) is gratefully acknowledged. Technical assistance and discussions with Prof. J. T. Gerig, Dr. Steve Hammond, and Curt Brenneman are greatly appreciated.

Registry No. 1 ($R = R_3 = CH_3$; $R_1 = CH_2CH(CH_3)_2$; $R_2 = H$), 87783-73-1; 1 ($R = R_3 = CH_3$; $R_1 = CH_2Ph$; $R_2 = H$), 87783-75-3; 1 (R = CH=CHPh; $R_1 = CH_2Ph$; $R_2 = H$; $R_3 = CH_3$), 87783-76-4; 1 (R = Ph; $R_1 = CH_2Ph$; $R_2 = H$; $R_3 = CH_3$), 87783-79-7; 1 ($R = CH_3$; $R_1 = CH_2Ph$; $R_2 = CH_2CBr{=}CH_2$; $R_3 = CH_3$), 87783-94-6; 1 ($R = CH_3$; $R_1 = CH_2CH(CH_3)_2$; $R_2 = H$; $R_3 = Ph$), 87783-88-8; 1 ($R = CH_3$; $R_1 = CH_2CH(CH_3)_2$; $R_2 = CH_2Ph$; $R_3 = CF_3$), 87783-64-0; 1 ($R = CH_3$; $R_1 = CH_2CH(CH_3)_2$; $R_2 = H$; $R_3 = CF_3$), 87784-00-7; 1 ($R = H$; $R_1 = CH_2CH(CH_3)_2$; $R_2 = H$; $R_3 = t$-Bu), 87783-83-3; 1 (R = CH=CHPh; $R_1 = R_2 = H$; $R_3 = CH_3$), 87783-77-5; 1 ($R = R_3 = CH_3$; $R_1 = H$; $R_2 = CH_2Ph$), 87783-90-2.

Benzopentathiepins: Synthesis via Thermolysis of Benzothiadiazoles with Sulfur†

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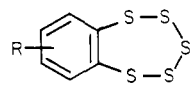
A general synthesis of benzopentathiepins has been developed by the thermolysis of benzothiadiazoles with sulfur. Dabco was found to enhance the yield of benzopentathiepin by approximately 2-fold. The scope and limitations of the method are also discussed.

Introduction

Polysulfides have been of great interest owing to their diversity in nature and their biological activity.[1] Some fundamental studies concerning sulfide exchange[2] and sulfur–sulfur bond cleavage processes in linear polysulfides[3] have recently appeared. Most of the synthetic work in this area has been limited to the construction of linear polysulfides[4] although some synthetic cyclic polysulfides have been described.[5] We became interested in cyclic polysulfides with five contiguous sulfur atoms, the benzopentathiepins **1**, and were intrigued by the fact that cyclic



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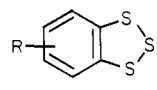
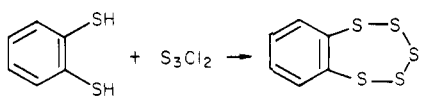


2

polysulfides fused to a benzene ring have been synthesized in both the pentathiepin[5a,6] and the trithiole[7] (**2**) forms. We want to address two fundamental questions: first, what are the factors which control the polysulfide ring size, and second, can we observe equilibration between these and other benzopolysulfide species? To probe these questions, a series of benzopentathiepins would be required. The methodology for benzopentathiepin preparation is severely limited. The only useful synthesis is due to Fehér[5a,6] (eq 1), although the sulfur monochloride route to an isothiazolopentathiepin might be applicable.[8] Both of these methods require a vicinal dithiol and since substituted benzene *o*-dithiols are not readily available, we desired a more general route to benzopentathiepins which avoided this intermediate.



(1)

The thermal decomposition of 1,2,3-benzothiadiazoles at 200–230 °C has been known for over 90 years.[9] Recently, it was reported that the pyrolysis temperature could be lowered to 80–120 °C by using di-*tert*-butyl peroxide as an initiator.[10] The intermediates from the thermolysis

† Contribution number 3327.

(1) See, for example: Still, I. W. J.; Kutney, G. W. *Tetrahedron Lett.* **1981**, *21*, 1939–1940. Morita, K.; Kobayashi, S. *Chem. Pharm. Bull.* **1967**, *15*, 988; *Tetrahedron Lett.* **1966**, 573. Wratten, S. J.; Faulkner, D. J.; *J. Org. Chem.* **1976**, *41*, 2465. Rahman, R.; Safe, S.; Taylor, A. *J. Chem. Soc. C* **1969**, 1665. Brewer, D.; Rahman, R.; Safe, S.; Taylor, A. *J. Chem. Soc., Chem. Commun.* **1968**, 1571.

(2) Whitesides, G. M.; Houk, J.; Patterson, M. A. K. *J. Org. Chem.* **1983**, *48*, 112–115 and references cited therein.

(3) Harpp, D. N.; Smith, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 6045–6053.

(4) Tsurugi, J.; Nakabayashi, T. *J. Org. Chem.* **1959**, *24*, 807–810. Nakabayashi, T.; Tsurugi, J.; Yabuta, T. *Ibid.* **1964**, *29*, 1236–1238. Reid, E. E. "Organic Chemistry of Bivalent Sulfur"; Chemical Publishing Co.: New York, 1960; Vol. III, pp 387–389.

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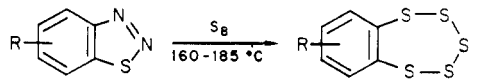
(9) Jacobsen, P.; Ney, E. *Chem. Ber.* **1889**, *22*, 904. Jacobsen, P.; Janssen, H. *Liebigs Ann. Chem.* **1893**, *277*, 218.

(10) Montevecchi, P. C.; Tundo, A. *J. Org. Chem.* **1981**, *46*, 4998–4999.

0022-3263/84/1949-1221$01.50/0

Table I. Synthesis of Benzopentathiepins



entry	R	equiv Dabco	% yield	mp, °C
1	H	0	35	58-60[e]
2	H	0.1	44	
3	H	1.0	54	
4	H	2.0	39	
5	6-Cl	0	22	87.5-89
6	6-CF_3 [a]	0	31	59-60
7	5-OCH_3	0	34	97-98
8	5-OCH_3	1.0	57	
9	5-$N(CH_3)_2$	0	45	121.5-122.5
10	4-Br	0	14	101-101.5
11	4-Br	1.0	22	
12	4-CF_3 [b]	0	20	61-62
13	7-Cl	0	0	
14	4,7-CH_3-6-Cl [c]	0	0	
15	5-CN	0	0	
16	5-NO_2	0	*d*	
17	5-NH_2	0	*d*	

[a] New compound, mp 40-42 °C. [b] New compound, mp 49-51 °C. [c] New compound, mp 81-82 °C. [d] Low yield of benzopentathiepin was obtained in impure form and detected by high-resolution mass spectroscopy. [e] Literature[5a] mp 65-66 °C.

of thiadiazoles[11a] (diradical, benzene episulfide, or thioketocarbene) have been reported to react by three modes: loss of sulfur, rearrangement to thioketene, and dimerization.[11b] The only external reagents which have successfully trapped the intermediates are those containing carbon–sulfur double bonds.[12] We postulated that elemental sulfur might be a suitable trap which could lead directly to benzopolysulfides. We report here the sulfur-induced thermolysis of 1,2,3-benzothiadiazoles to prepare benzopentathiepins.

Results

When 1,2,3-benzothiadiazole was heated to 195 °C in decalin for 1 h, no reaction occurred. In contrast, when an equivalent of sulfur was present, nitrogen was evolved at 160 °C to 170 °C. The gas evolution ceased within 1.5 h and workup gave a mixture of sulfur, benzopentathiepin, and organic sulfur polymer. Silica gel chromatography removed the polymeric material but could not completely separate the sulfur and the pentathiepin. Medium- or high-pressure liquid chromatography completed the purification to give a 34% yield of crystalline benzopentathiepin with spectral properties identical with those reported;[5a] *m/e* 235.8914 (calcd *m/e* for $C_6H_4S_5$, 235.8917).

A series of 1,2,3-benzothiadiazoles (Table I) was prepared to examine the scope of this novel reaction. These materials were prepared by using standard methodology[13] with 4-(trifluoromethyl)-1,2,3-benzothiadiazole[14] being the only exception. This new compound was prepared from 4-bromo-1,2,3-benzothiadiazole by using the recently developed trifluoromethylation reaction of Matsui and co-workers.[15] Table I shows the results of the thermolysis of these benzothiadiazoles with sulfur. The process is general as both electron-donating and -withdrawing substituents can be tolerated. Only substituents which react with sulfur (or some activated form of sulfur generated under the reaction conditions) such as CH_3, NH_2, and CN fail to give a benzopentathiepin product. A further limitation is that 7-substituents inhibit the reaction. Because of the product symmetry, however, the 4-substituted benzothiadiazoles provide the same 6-substituted benzopentathiepin products. The effect of 7-substituents suggests that the reaction is initiated by attack of some external species on the sulfur atom of the benzothiadiazole.

We attempted several modifications of this reaction with no improvement in the yield.[16] Then our attention was drawn to the significantly higher yield of pentathiepin with 5-(dimethylamino)-1,2,3-benzothiadiazole. This observation led us to examine tertiary amine catalysis. Diazabicyclo[2.2.2]octane (Dabco) had a pronounced effect on the thermolysis (entries 1–4, Table I). The effect was maximized with 1 equiv of Dabco and the yield of benzopentathiepin was increased to 54% compared with 35% for the uncatalyzed reaction. Dabco generally appears to about double the yields of benzopentathiepins (entries 3, 8, 11, Table I). Unlike Dabco, however, other amines did not enhance the yields of pentathiepins. In fact most amines lowered the yields (see Table II). These yield losses can be attributed to reactions of the amines with the benzopentathiepin products. For example, in control experiments where 7-chlorobenzopentathiepin was heated for 1 h at 165 °C with an equivalent of amine, 50% of 7-chlorobenzopentathiepin was recovered from the reaction with Dabco, but only 10% was recovered from the reaction with tributylamine. Interestingly, the presence of an amine in the thermolysis reaction did not increase the rate of reaction of the 1,2,3-benzothiadiazole. A partial conversion study showed that benzothiadiazole reacted with sulfur at 170 °C at comparable rates with no amine, with Dabco, and with tributylamine. If anything, the presence of amine slightly retarded thermolysis.

Table II. Effect of Amines on Benzopentathiepin Yield[a]

amine	% yield
none	35
Dabco	54
DBU	12
n-Bu_3N	2.3
n-Pr_3N	2.3
Ph_3N	20
4-(dimethylamino)pyridine	33

[a] All reactions run with 1 equiv of amine at 160-185 °C until N_2 evolution ceased (0.5-1.5 h).

(11) (a) Krantz, A.; Laureni, J. *J. Am. Chem. Soc.* **1981**, *103*, 486–496 and references cited therein. (b) This statement is not meant to imply that all of these possible intermediates are present nor that each one reacts by all three modes.

(12) Hünig, S.; Fleckenstein, E. *Liebigs Ann. Chem.* **1970**, *738*, 192–194. Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565. Davidson, S.; Leaver, D. *J. Chem. Soc., Chem. Commun.* **1972**, 540–541.

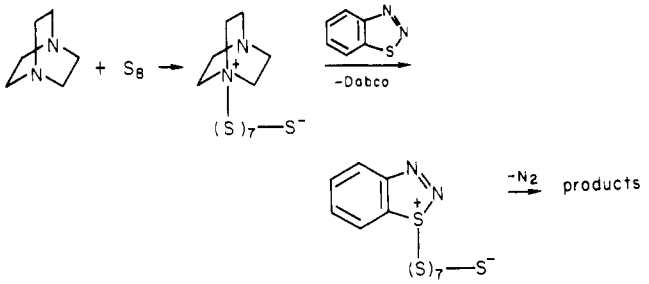
(13) For a general review of 1,2,3-benzothiadiazole synthesis see: Lionel, G. D. PhD Dissertation, Cornell University, 1973.

(14) All new compounds gave acceptable analytical and/or high-resolution mass spectral data.

(15) Matsui, K.; Tobita, E.; Ando, M.; Kondo, K. *Chem. Lett.* **1981**, 1719–1720.

(16) Modifications of the thermolysis reaction were carried out on equimolar amounts of benzothiadiazole and sulfur (as S_8) under the following sets of conditions: (a) Free radical catalysis was attempted at a temperature where the half-life for the initiator was ca. 100 min. In all cases only trace amounts of benzopentathiepin were observed. Initiator, $t_{1/2}$, reaction temp: AIBN, 70 min (80 °C), 80 °C; *tert*-butylperbenzoate, 100 min (120 °C), 120 °C; *tert*-butylperacetate, 100 min (118 °C), 120 °C; benzoyl peroxide, 100 min (90 °C), 90 °C; azodicyclohexane carbonitrile, 100 min (100 °C), 100 °C. Catalysis with di-*tert*-butyl peroxide was attempted at 120 °C and 160 °C. (b) Photochemical stimulation was attempted at 300 nm in a Rayonet reactor at 3×10^{-2} M S_8 and 4×10^{-3} M benzothiadiazole in benzene and chloroform. Benzothiadiazole has an absorption at 310 nm (ϵ 2500) and sulfur has end absorption ($\epsilon \sim 2000$) at 300 nm. Only polymeric sulfur precipitate was observed. (c) Acid catalysis was attempted with *p*-toluenesulfonic acid with no benzopentathiepin observed. (d) Active sulfur transfer agent: When ca. 10 mole % benzimidazole disulfide was added to the reaction at 170 °C a 10% yield of benzopentathiepin was obtained.

Scheme I. Possible Dabco Interaction



Discussion

Although a detailed mechanism for the formation of benzopentathiepins cannot be ascertained at this time, the following observations are pertinent. Since benzothiadiazole is stable up to 195 °C in the absence of sulfur, sulfur or some activated form of sulfur must promote the thermolysis of benzothiadiazole. The site of the interaction appears to be the thiadiazole sulfur atom because 7-substituted benzothiadiazoles are inert whereas the 4-substituted derivatives readily react. Montevecchi and Tundo have proposed a similar activation scheme for their radical-catalyzed decomposition of benzothiadiazoles to give thianthrenes.[10]

The yield of benzopentathiepin is little affected by solvent polarity (34%, 30.5%, and 29% yields in decalin, nitrobenzene, and dimethyl sulfoxide, respectively), although the reaction appears to proceed much more slowly in the polar solvents (3–4 vs. 0.5–1 h in decalin). The reaction cannot be facilitated with radical initiators including AIBN, di-*tert*-butyl peroxide, *tert*-butyl peracetate, and others.

There are several possible explanations for the improved yield of benzopentathiepin when Dabco is used. First, since Dabco is known to give a very stable radical cation,[17] it might facilitate the reaction by an electron-transfer process. However, this is unlikely because other electron-transfer agents such as triphenylamine decrease the yield (Table II).

It is possible that Dabco stabilizes the product benzopentathiepin toward decomposition at the reaction temperatures. Finally, although there is no compelling evidence, an ionic mechanism as in Scheme I similar to the one suggested recently by Tebbe, Wasserman, and coworkers[18] for the equilibration of S_8 with S_7 and S_6 cannot be dismissed.

Summary

We have developed a new general synthesis of benzopentathiepins from benzothiadiazoles and defined the scope and limitations of the method. Dabco enhances the yield of benzopentathiepin by approximately 2-fold. A variety of substituted benzopentathiepins are now available for further study. The properties and reactivities of these interesting molecules, as well as extensions of this chemistry to heterocyclic polysulfides, will be the subjects of future reports in this area.

Experimental Section

General Procedures. Melting points were taken with a Thomas Hoover or a Buchi capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet 7199 FT infrared spectrometer and are reported in reciprocal centimeters. Only strong bands are reported unless otherwise stated. Routine proton NMR were obtained at either 80 or 90 MHz with a Varian EM390 or an IBM NR80 FT instrument. NMR data are reported in parts per million (δ) downfield from tetramethylsilane in deuteriochloroform. Analyses were determined by either Micro-Analysis Inc., Wilmington, DE, or our own analysis group.

4-(Trifluoromethyl)-1,2,3-benzothiadiazole. 4-Bromo-1,2,3-benzothiadiazole (5.0 g, 23.2 mmol) was dissolved in *N*-methylpyrrolidinone (200 mL, freshly distilled from CaH_2), and sodium trifluoroacetate [8.5 g, 62.5 mmol, dried 24 h at 25 °C (0.1 mm)] and cuprous iodide [8.75 g, 46 mmol (Alpha, ultrapure)] were added. The mixture was heated to 160 °C for 4 h (gentle CO_2 evolution), cooled, and diluted carefully with water (300 mL). The slurry was filtered through Celite and the pad was rinsed with ether (3 × 250 mL). The filtrate phases were separated and the organic layer was washed with water and brine; then it was filtered through a cone of calcium sulfate and concentrated. The crude product was chromatographed on Silica Woelm TSC (500 g, 15% ether–hexane) to give first a mixture of 4-bromo-, 4-iodo-, and 4-(trifluoromethyl)-1,2,3-benzothiadiazoles followed by pure 4-(trifluoromethyl)-1,2,3-benzothiadiazole. The mixed fraction was rechromatographed on the same column to give additional pure product. In this manner 3.19 g (67%) of 4-(trifluoromethyl)-1,2,3-benzothiadiazole was obtained as an off-white solid, mp 41–44 °C. A sample further purified by sublimation at 45 °C (10–20 mm, water aspirator) had mp 49–51 °C; NMR δ 8.35 (d, J = 8 Hz, 1 H), 8.0 (d, J = 8 Hz, 1 H), 7.8 (t, J = 8 Hz, 1 H); IR (KBr) 1319, 1152, 1122, 1089; ^{19}F NMR δ −58.78 (s).

Anal. Calcd for $C_7H_3F_3N_2S$: C, 41.18; H, 1.48; N, 13.72. Found: C, 41.13; H, 1.37; N, 13.96.

6-(Trifluoromethyl)-1,2,3-benzothiadiazole. 2-Chloro-4-(trifluoromethyl)nitrobenzene (20 g, 88.6 mmol) was dissolved in dimethyl sulfoxide (100 mL, dried over molecular sieves) under a nitrogen atmosphere, and anhydrous sodium sulfide (6.92 g, 88.6 mmol) was added all at once. The mixture warmed to ~40 °C and was stirred for 2 h. The red mixture was poured into a solution of brine (300 mL) and 6 N HCl (100 mL) and extracted with methylene chloride (3 × 100 mL). The combined organic phase was filtered through a cone of sodium sulfate and concentrated to leave 18.46 g of yellow solid.

Nitrogen was bubbled through deionized water (400 mL) for 15 min; then the above yellow solid and ammonium hydroxide (90 mL) were added. Sodium hydrosulfite (90 g) was dissolved in deionized water (400 mL) and added to the mechanically stirred reaction over 10–15 min via an addition funnel. The resulting solution was warmed to 50 °C for 3 h and then stirred overnight at ambient temperature. The mixture was acidified to pH 7 with acetic acid and extracted with ether (3 × 200 mL). The combined organic layer was washed with brine and filtered through a cone of calcium sulfate into a flask equipped with mechanical stirring and a gas inlet. Hydrogen chloride was bubbled through the stirred solution for 1.5 h. The solid was filtered, rinsed with dry ether, and dried in vacuo to give 8.96 g of tan hydrochloride salt: mp 184–188 °C; IR (KBr) 1330 cm^{-1}.

The above salt was slurried in 5% aqueous HCl (100 mL) and chilled to 0 °C. A solution of sodium nitrite (3.22 g) in water (15 mL) was added dropwise over 20 min to the stirred mixture; then it was neutralized to pH 9 with 20% aqueous sodium hydroxide. The reaction was extracted with ether (3 × 100 mL), and the organic phase was washed with water and brine and then filtered through a cone of sodium sulfate. Concentration left 6.94 g of a brown oil which was chromatographed on silica gel (250 g, 10% ether–hexane) to give, after a 350-mL forerun, a trace of impurity in 250 mL and then 2.35 g of 6-(trifluoromethyl)-1,2,3-benzothiadiazole in 150 mL of eluent. A sample sublimed at 25 °C (0.15 mm) had mp 40–42 °C; NMR (90 MHz) δ 8.9 (m, 1 H), 8.25 (dd, 1 H), 7.9 (ddd, 1 H); IR (KBr) 1332, 1294, 1192, 1150 (sh), 1129 cm^{-1}.

Anal. Calcd for $C_7H_3F_3N_2S$: C, 41.18; H, 1.48; N, 13.72. Found: C, 41.31; H, 1.51; N, 13.56.

Benzopentathiepins. The following illustrates our general procedure for preparing benzopentathiepins. Sulfur (1 equiv as S_8), 1,2,3-benzothiadiazole (1 equiv), Dabco (1 equiv if used), and decalin (10 mL per gram of benzothiadiazole) were combined

(17) McKinney, T. M.; Geske, D. H. *J. Am. Chem. Soc.* **1965**, *87*, 3013–3014.

(18) Tebbe, F. N.; Wasserman, E.; Peet, W. G.; Vatvars, A.; Hayman, A. C. *J. Am. Chem. Soc.* **1982**, *104*, 4971–4972.

under a static nitrogen atmosphere with a gas bubbler. The mixture was heated to the temperature where nitrogen evolution was steady (typically 160–190 °C) until the gas evolution ceased (20 min–1.5 h). The mixture was cooled and the decalin was removed by kugelrohr distillation [50 °C (0.5 mm)]. The residue was triturated with methylene chloride twice and filtered to remove sulfur. The solution was then concentrated onto silica gel and chromatographed on the same with ether–hexane (typically 1% ether) to obtain in most cases the benzopentathiepin contaminated with sulfur. The product was further purified by recrystallization and/or medium- (Lobar, Silica gel 60 Size C, hexane) or high-pressure (Zorbax Sil, hexane) liquid chromatography. This procedure has been successfully carried out on a 0.25–10 g scale.

Benzopentathiepin: 35% without Dabco; 54% with Dabco; mp 58–60 °C (hexane) (lit.[5a] mp 65–66 °C); NMR δ 7.85–7.7 and 7.45–7.2 (AA'BB' m); mass spectrum, m/e 235.8914; calcd m/e for $C_6H_4S_5$, 235.8917.

7-Chlorobenzopentathiepin: 22% without Dabco; mp 87.5–89 °C (hexane); NMR δ 7.9–7.7 (d, 2 H), 7.4–7.2 (m, 1 H); IR (KBr) 1095, 822 cm^{-1}; mass spectrum, m/e 269.8517; m/e calcd for $C_6H_3ClS_5$, 269.8527.

Anal. Calcd for $C_6H_3ClS_5$: C, 26.61; H, 1.12. Found: C, 26.84; H, 1.22.

7-(Trifluoromethyl)benzopentathiepin: 31% without Dabco; mp 59–60 °C (hexane); NMR δ 8.18 (d, J = 2 Hz, 1 H), 8.0 (d, J = 8 Hz, 1 H), 7.55 (dd, J = 2, 8 Hz, 1 H); IR (KBr) 1320 cm^{-1}; mass spectrum, m/e 303.8788; calcd m/e for $C_7H_3F_3S_5$, 303.8790.

Anal. Calcd for $C_7H_3F_3S_5$: C, 27.62; H, 0.99. Found: C, 27.92; H, 0.94.

7-(Dimethylamino)benzopentathiepin: 45% without Dabco; may be isolated pure from the column chromatography; mp 121.5–122.5 °C (ethanol); NMR δ 7.55 (d, J = 8.5 Hz, 1 H), 7.0 (d, J = 2.7 Hz, 1 H), 6.5 (dd, J = 8.5, 2.7 Hz, 1 H), 3.0 (s, 6 H); IR (KBr) 1583 cm^{-1}; mass spectrum, m/e 278.9343; calcd m/e for $C_8H_9NS_5$, 278.9338.

Anal. Calcd for $C_8H_9NS_5$: C, 34.38; H, 3.25; S, 57.36. Found: C, 34.21; H, 3.42; S, 56.99.

7-Methoxybenzopentathiepin: 34% without Dabco; 57% with Dabco; may be isolated pure directly from the column chromatography; mp 97–98 °C; NMR δ 7.75 (d, J = 8.3 Hz, 1 H), 7.3 (d, J = 2.7 Hz, 1 H), 6.8 (dd, J = 2.7, 8.3 Hz, 1 H), 3.85 (s, 3 H); mass spectrum, m/e 265.9011; m/e calcd for $C_7H_6OS_5$, 265.9022.

6-Bromobenzopentathiepin: 14% without Dabco; 22% with Dabco; mp 101–101.5 °C (hexane); NMR (360 MHz) δ 7.78 (dd, J = 1.3, 8.0 Hz, 1 H), 7.66 (dd, J = 1.3, 8.0 Hz, 1 H), 7.2 (t, J = 8.0 Hz, 1 H); IR (KBr) 788 cm^{-1}.

Anal. Calcd for $C_6H_3BrS_5$: C, 22.86; H, 0.96. Found: C, 23.09; H, 0.94.

6-(Trifluoromethyl)benzopentathiepin: 20% without Dabco; mp 61–62 °C (hexane); NMR δ 8.1 (long range coupled d, J = 8.0 Hz, 1 H), 7.85 (long range coupled d, J = 8.0 Hz, 1 H), 7.48 (long range coupled t, J = 8.0 Hz, 1 H).

Anal. Calcd for $C_7H_3F_3S_5$: C, 27.62; H, 0.99. Found: C, 27.65; H, 1.03.

Registry No. 1 (R = H), 17071-97-5; 1 (R = 7-Cl), 88888-94-2; 1 (R = 7-CF_3), 88888-95-3; 1 (R = 7-MeO), 88888-96-4; 1 (R = 7-Me_2N), 88888-97-5; 1 (R = 6-Br), 88888-98-6; 1 (R = 6-CF_3), 88888-99-7; $CF_3C(O)ONa$, 2923-18-4; Na_2S, 1313-82-2; S_8, 7704-34-9; Dabco, 280-57-9; 4-bromo-1,2,3-benzothiadiazole, 31860-00-1; 2-chloro-4-(trifluoromethyl)nitrobenzene, 402-11-9; 1-(trifluoromethyl)-3-mercapto-4-hydrazinobenzene hydrochloride, 88888-90-8; 1,2,3-benzothiadiazole, 273-77-8; 6-chloro-1,2,3-benzothiadiazole, 23644-01-1; 6-(trifluoromethyl)-1,2,3-benzothiadiazole, 88888-91-9; 5-methoxy-1,2,3-benzothiadiazole, 31860-05-6; 5-(dimethylamino)-1,2,3-benzothiadiazole, 88888-92-0; 4-(trifluoromethyl)-1,2,3-benzothiadiazole, 88888-93-1.

Pyrazolothiadiazoles from 3-Aminopyrazoles: The Hetero-Herz Reaction

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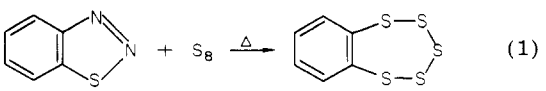
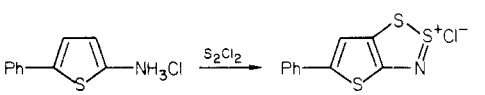
The reaction of sulfur monochloride with pyrazoleamines gives good to excellent yields of pyrazolodithiazolium chlorides from a hetero-Herz reaction. No chlorination of the pyrazole nucleus was observed—a normal occurrence in Herz reactions. The Herz salts were converted to novel pyrazolothiadiazoles.

We recently discovered a new reaction of 1,2,3-benzothiadiazoles with sulfur (eq 1) that results in the direct formation of benzopentathiepins.[1] To explore the scope



(1)

of this reaction, we required access to hetero-fused 1,2,3-thiadiazoles. The usual preparation of fused 1,2,3-thiadiazoles is by diazotization of *o*-amino thiols.[2] These thiols are available from *o*-chloronitrobenzenes, benzothiazoles, or by the Herz reaction[3] of anilines with sulfur monochloride. We perceived that heterocyclic amines would be the most easily accessible precursors and therefore we chose to examine the hetero-Herz reaction. While the Herz reaction with anilines has been extensively explored,[4] there has been surprisingly little work on its use with heterocyclic amines. There is one report on the preparation of a thiophene Herz salt (eq 2).[5] We report here the preparation of a series of 5-substituted 3-aminopyrazoles, their efficient conversion to pyrazolodithiazolium chlorides via the Herz reaction, and the preparation of novel pyrazolo-



(2)

† Contribution No. 3368 from the department.

(1) Chenard, B. L.; Miller, T. J. *J. Org. Chem.*, preceding paper in this issue.
(2) For an excellent review of benzothiadiazole synthesis, see: Lionel, G. D., Ph.D. Dissertation, Cornell University, 1973.
(3) L. Cassella and Co.; German Patents 360 690, 364 822, 367 344, 367 345, 367 346, 370 845.
(4) Warburton, W. K. *Chem. Rev.* **1957**, 1011–1120.
(5) Abramenko, P. I.; Ponomareva, T. K.; Priklonskikh, G. I. *Khim. Geterotsikl. Soedin.* **1979**, *4*, 477–480.

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